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Quantum dynamics of photodetachment of electrons from halide ions : a time – dependent Fourier grid Hamiltonian method based study

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Abstract · We model the electronic states of halide ions (X^-) by a one – dimensional potential $V(x) = -V_0 e^{-\sigma x^2}$ Environmental perturbation is sought to be taken into account by introducing random fluctuations in the well depth (V_0) of the model halide ion Dynamics of detachment of electrons from X is followed by numerically solving the time – dependent Schrodinger equation for the model hamiltonian $H(x, t) = \frac{p_x^2}{2m} - V_0 \{1 + \Delta V R(t)\} e^{-\sigma x^2} - \varepsilon x \sin(\omega t)$, ε being the intensity of radiation of frequency ω, ΔV the strength of fluctuation and $R(t)$ being either - 1 or 1 randomly The ionization rates, thresholds and their modulation by environmental perturbations are studied

Keywords Fourier grid method, photodetachment of electrons, halide ions

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1. Introduction

Halide ions are among the most stable atomic anionic species and can exist freely in aqueous solutions. Electron detachment from them by light is an interesting event as it involves destruction of a charged species (X^-) creating a neutral one (X)with the simultaneous ejection of an electron (e^-). The leaving electron feels only the potential of a neutral atom (X). The coupling between the electron and the neutral atom is weak and can be described by a rather short range potential. That enables one to study these system in great detail.

Anionic photodetachment investigations have been pursued both theoretically [1-5] and experimentally [6,7] for a number of reasons. Among them are (i) it provides a unique and precise method for determining binding energies of anionic species, (ii) photodetachment provides a source of continuous opacity in the visible and IR spectra of hot gases and stellar atmosphere. It may be mentioned here that electron detachment from anions can also be triggered by static electric fields and theories of negative ion decay in such situations are

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available in literature. The most elementary among these theories is asymptotic in the parameter $s_0 = 2\frac{(2E_b)^{\frac{3}{2}}}{3\varepsilon}$ where E_b is the electron affinity of X and ε is the strength of the electric field. More refined theories are also available. Light induced electrondetachment is a dynamical event and can be followed by setting up and solving the appropriate Schrodinger equation for the system concerned. For the halide ions we propose to do it in 2 steps : first, we model the ions by suitable 1-d potentials (this involves solving energy eigenvalue equation for the model ions by the Fourier Grid Hamiltonian (FGH) method [8] with a view of fixing the parameters of the model) and next, we solve the time – dependent Schrodinger equation for the system perturbed by the electric field of light. We invoke the time-dependent Fourier Grid Hamiltonian (TDFGH) method developed by us earlier [9-12] for the second step.

2. The model

The systems of our concern are halide ions (X^-, $X = Cl, Br, I$) in their respective ground states which are spherically symmetric ($l = 0$) states. We model the states by the states of an electron moving in a $1-d$ potential $V(x) = -V_0 e^{-\sigma x^2}$ $(-\infty \le x \le \infty)$ The parameters of the model potential (MP) are V_0 (well-depth) and $\sigma^{1/2}$ (width of the well). They are fixed by demanding that $V(x)$ must reproduce the ground state ionization potential of the halide ion that it seeks to model.

The coupling of the halide ion with the environment inevitably brings in random perturbations in the system which are sought to be modelled by allowing the well depth (V_0) to fluctuate randomly

$$V(x, t) = -V_0\{1 + \Delta V\, R(t)\} e^{-\sigma x^2},$$

$$= -V_0\{1 + V'(t)\} e^{-\sigma x^2}. \tag{1}$$

ΔV in eq. (1) represents the strength of fluctuation while $R(t)$ is allowed to take on values +1 or – 1 randomly. Hence, $< V'(t) > = 0$.

The full hamiltonian of the model anion perturbed by light of frequency ω and intensity ε is given by

$$\hat{H}(x, t) = \frac{p_x^2}{2m} - V_0\{1 + \Delta V\, R(t)\} e^{-\sigma x^2} - \varepsilon\, x \sin(\omega t),$$

$$= \frac{p_x^2}{2m} - V_0\, e^{-\sigma x^2} - \Delta V\, V_0\, R(t) e^{-\sigma x^2} - \varepsilon\, x \sin(\omega t),$$

$$= H_0 + V(x, t), \tag{2}$$

and the time dependent Schrödinger equation (TDSE) to be solved is

$$\hat{H}\psi(x, t) = i\hbar \frac{\delta \psi(x, t)}{\delta t}. \tag{3}$$

At $t = 0$, we have,

$$\hat{H}(x, 0) = \frac{P^2}{2m} - V_0\{1 + \Delta V\, R(0)\} e^{-\sigma x^2}. \tag{4}$$

If we set $R(0) = 0$,

$$\hat{H}(x, 0) = \frac{P^2}{2m} - V_0\, e^{-\sigma x^2} = H_0, \tag{5}$$

that is, at $t = 0$ we have the completely unperturbed model halide ion. H_0, therefore defines the initial states of the model, and the time evolution of the system described by $H(x, t)$ can be obtained by numerically integrating eq. (3) by the TDFGH method.

3. The method

Let us start with the TDSE of equation (3). We can employ the FGH method [8] to compute the eigenfunctions and eigenvalues of H_0 representing the unperturbed halide ion at t = 0, giving

$$H_0 \left|\phi_i^0(x)\right\rangle = \varepsilon_i^0 \left|\phi_i^0(x)\right\rangle, i = 1, 2, \ldots, N, \tag{6}$$

where $N = 2n + 1$ is the number of grid points used for representing $\left|\phi_i^0\right\rangle$ in the coordinate space. In the FGH recipe, we have

$$\left|\phi_i^0\right\rangle = \sum_{p=1}^{N} \left|x_p\right\rangle \Delta x W_{pi}^0 \tag{7}$$

with the grid orthonormality condition $\left\langle x_p \mid x_q \right\rangle \Delta x = \delta_{pq}$. W_{pi}^0's in eq. (7) represents the value of the coordinate representative of the eigenfunction $\left|\phi_i^0(x)\right\rangle$ of H_0 at the p-th grid point and are obtained by the now standard variational route. The FGH method can be used to propagate the wave function on the same grid. Thus at $t > 0$, when the perturbation due to the radiation and well – depth fluctuations are turned on, the state function $\left|\psi(x,t)\right\rangle$ is supposed to be represented by

$$\left|\psi(x,t)\right\rangle = \sum_{p=1}^{N} \left|x_p\right\rangle \Delta x W_p(t). \tag{8}$$

The grid point amplitudes $W_p(t)$ are now time-dependent and their evolution equations can be found out by making appeal to the Dirac – Frenkel variational principle : $\left\langle \partial\psi \mid H - i\frac{\partial}{\partial t} \mid \psi \right\rangle = 0$ which gives the following set of evolution equations for W_p's.

$$\dot{W}_p = \frac{1}{i\hbar} \sum_{q=1}^{N} \left[\left\langle x_q \left| H_0 \right| x_p \right\rangle + \left\langle x_q \; -V_0 \Delta V e^{-\sigma x^2} - \varepsilon x \sin(\omega t)\; x_p \right\rangle \right] W_q(t)$$

$$(for\, p = 1, 2, \ldots\ldots, N) \tag{9}$$

Once, initial values of $W_q(t)$'s are available, the eq. (9) can be numerically integrated. The matrix elements in eq. (9) are evaluated easily :

$$\langle x_p | H_0 | x_q \rangle = \frac{1}{\Delta x}\left[\sum_{l=-n}^{+n} \frac{\exp\left[\frac{2\pi i(p-q)}{n}\right]}{N}\right] T_l - V_0 e^{-\sigma x_p^2}\delta_{pq}, \tag{10}$$

where T_l in eq (10) is given by

$$T_l = \left[\frac{\hbar^2}{2m}\right](l\Delta k)^2, \text{ with}$$

$$\Delta k = \frac{2\pi}{N\Delta x}, N = 2n+1. \tag{11}$$

When $W_p(t)$'s and hence $|\psi(x,t)\rangle$ are obtained, the projections of $|\psi(x,t)\rangle$ on the unperturbed eigenstates of H_0 give us time – dependent overlap amplitudes $[S_l(t)]$.

$$S_l(t) = \langle \phi_l^0(x,0) | \psi(x,t)\rangle, l = 1,2,\ldots N. \tag{12}$$

$|S_l(t)|^2$ represents the population of the l-th state of the unperturbed system (or it's survival probability) at a time t after the perturbation have been turned on. The probability of ionization at a time T is then given by

$$P_I(T) = 1 - \sum_{l=1}^{n_b} |S_l(T)|^2, \tag{13}$$

where n_b is the number of bound states supported by H_0. The slopes of the plots of $ln\ P_I(t)$ against t then give us the rate constants of ionization.

4. Results and discussion

Detailed calculations have been carried out on a model Chloride ion (Cl^-) for which V_0 and σ were chosen to have the values 6.197 *e.v.* and 0.1240 (a_0^{-2}), respectively from a calibrating calculation. The TDFGH calculations were performed on a grid of length 15 *a.u.* and 100 points. The applied radiation was a continuous wave at frequency ω where $\hbar\omega = 0.06$ *a. u.*. Numerical integration was carried out by 4th order Runge – kutta with small time steps (1000 time steps = 0.5 *fs*). We present the results under three different headings :

(i) Population dynamics :

Figure 1 shows population dynamics when the free model halide ion (fixed well depth) interacts with a monochromatic radiation ($\varepsilon = 0.03$ $\hbar\omega = 0.06$, all in atomic units). The ground state population or survival probability (S_1) decreases monotonically for a little more than 10 *fs* while the population in the excited levels (S_2 to S_4) rises and falls systematically and sequentially because of coherent interaction with the radiation. Since the potential supports only one

bound state, any excitation into $n > 1$ levels signify onset of ionization. The time – dependent ionization probability from the ground state of Cl^- ion is then given by $(1 - S_1(t))$ (cf. eq. 13). The ionization probability (P_I) is plotted in Figure 2 against time. There appears to be a very

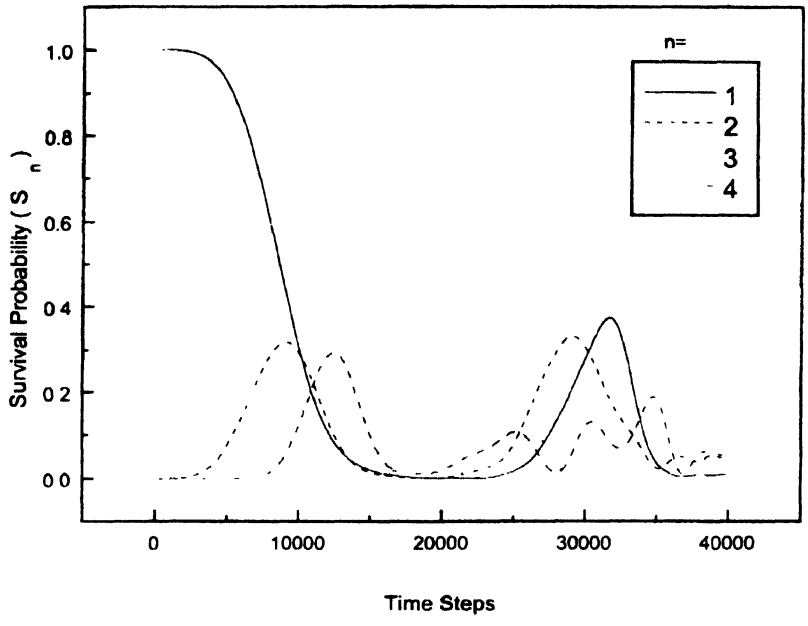

Figure 1. Polulation dynamics in a model chloride ion perturbed by light of fairly high intensity (ε = 0.025 a.u.)

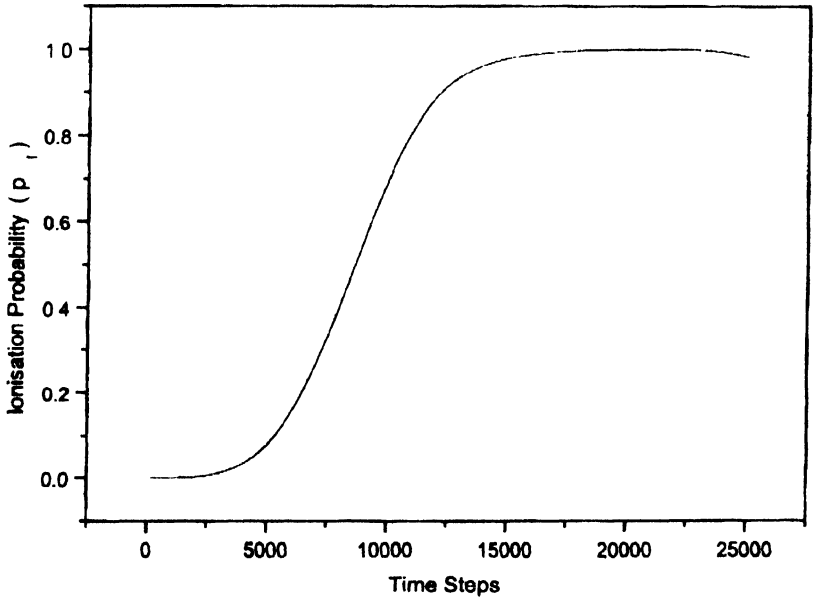

Figure 2. Photoionization probability of a model chloride ion from ground state shown as a function of time.

small time lag (~ $1 fs$) between the incidence of radiation and the onset of ionization which is nearly complete in about $9 fs$ at the given level of intensity.

(ii) Ionization rate constant and its ε dependence :

From the $P_I - t$ profile and the relation $\frac{d}{dt}(\ln P_1) = k_\varepsilon(t)$, we have calculated the instantaneous ionization rate constant, $k_\varepsilon(t)$. The average of $k_\varepsilon(t)$ over the entire time – span of observation is k_ε which is plotted against the light intensity in Figure 3. The mean – ionization rate constant turns out to have a strong non- linear dependence on intensity of light. It shows saturation at high intensities, a feature that has been observed experimentally also. If electron detachment occurs by absorption of n – photons, standard perturbation theory would predict that the yield of electron would increase as the n-th power of the incident flux. The power law behaviour can be replaced by saturation in high power domain when the depletion of the initial state is non-negligible.

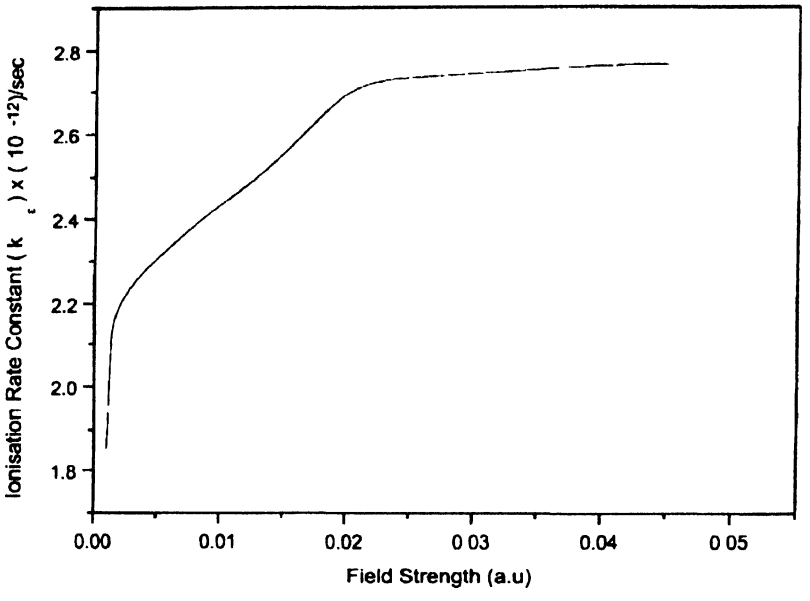

Figure 3. Field-dependence of mean photoionization rate constant from the ground state of chloride ion. Note the saturation at higher field strengths.

(iii) Environmental perturbation of k_ε:

We have indicated at the beginning that a fluctuating well-depth can be introduced to mimic the effects of random environmental perturbation on the ionization process. Figures 4 and 5 depict how k_ε responds to variations in the fluctuation frequency (ω) and fluctuation strength (ΔV), respectively. k_ε clearly passes through a minimum when plotted as a function of ω for a fixed value of ΔV. This would seem to imply that the anion–decay may be suppressed by environmental noise, if its frequency is in a specific range. If ω lies the specified range, the increase of fluctuation strength further suppresses the ionization rate (Figure 5). Thus, an

incoherent perturbation produced by the environment may sometimes mask the effects of coherent perturbation provided by the radiation field. A 3-dimensional extension of the present model is in progress.

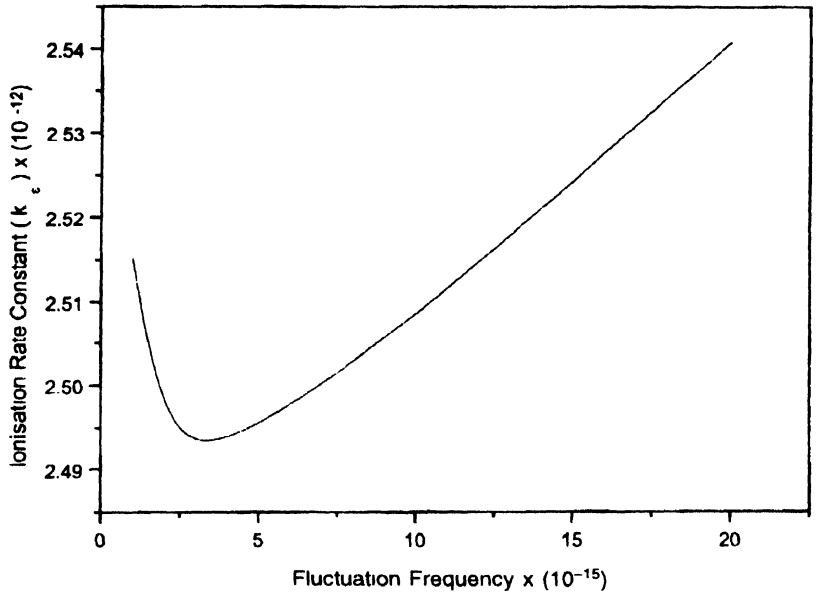

Figure 4. Dependence of photoionization rate constant (Cl) on the well-depth fluctuation frequency (Ω) Note the suppression of ionization at low Ω

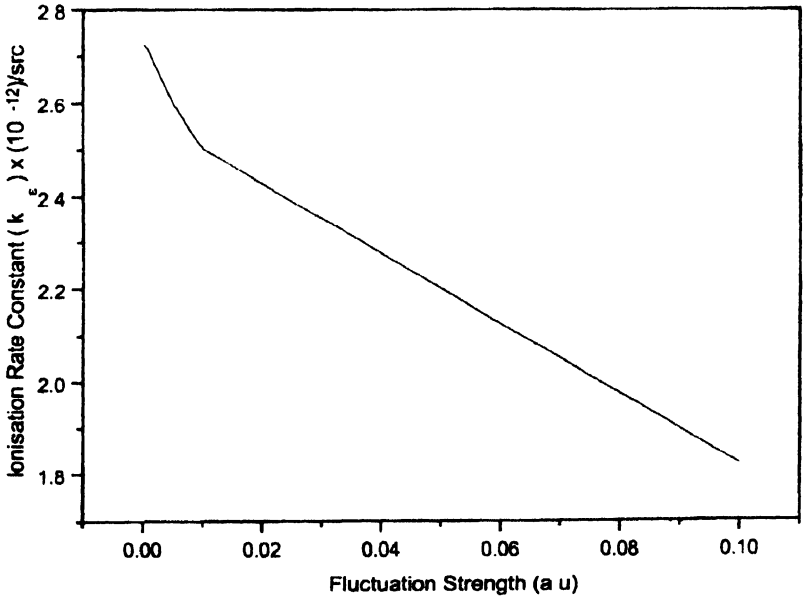

Figure 5. Decrease of photoionization rate constant (Cl^-) as a function of fluctuation strength.

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